Guidelines for sampling and determination of hydrogen sulphide (H_2S) in Seawater

1. Background

1.1 Introduction

Hydrogen sulphide is a poisonous gas that readily dissolves in water. The sulphide is formed in stagnant waters, where the oxygen has been consumed by bacteria oxidizing organic matter to carbon dioxide, water, and inorganic ions. Sulphate-reducing bacteria then use the oxygen bound in sulphate ions as an electron acceptor while reducing the sulphate ions to sulphide. No higher life forms can exist in water containing hydrogen sulphide, and these areas are thus turned into oceanic deserts. Hydrogen sulphide in a water sample is easily detected by its characteristic smell, even at concentrations lower than those measurable with the method below.

1.2 Purpose and aims

Monitoring of dissolved oxygen and hydrogen sulphide provide information of an indirect effect of eutrophication. The purpose of the monitoring is to map the spatial distribution of concentrations of dissolved oxygen and hydrogen sulphide, with the aim to be able to assess the status of the seafloor and the waters above and to ensure that the data is comparable for the HELCOM pre-core indicator 'Shallow-water oxygen' and core indicator 'Oxygen debt'. The indicator descriptions, including their monitoring requirements, are given in the HELCOM core indicator web site: http://helcom.fi/baltic-sea-trends/indicators/oxygen.

2. Monitoring methods

2.1 Monitoring features

The monitoring of hydrogen sulphide is done in combination with dissolved oxygen measurements to assess the level of oxygen depletion.

2.2 Time and area

The oxygen/hydrogen sulphide should be monitored a few times per year, particularly in critical areas and season (e.g. the late summer/autumn).

2.3 Monitoring procedure

2.3.1 Monitoring strategy

The reference method for sampling and determination of hydrogen sulphide in the Baltic area is the spectrophotometric method described in Fonselius et al. (1999). This book should be consulted for exact reagent compositions and procedures. For concentrations up to approximately 250 µM, the method by Fonselius et al. (1999) is recommended. Samples containing higher concentrations may be diluted after precipitation with a zinc acetate solution containing 2 g l-1 of gelatine (Grasshoff and Chan, 1971). This solution can be homogenized and diluted. However, higher levels of sulphide are better quantified using the method by Cline (1969).

Minimum analytical requirements: hydrogen sulphide can be detected, although not quantified, by smelling the water sample.

Subsampling for hydrogen sulphide analysis is to be conducted when hydrogen sulphide smell occurs or if oxygen levels are low. Water samples are collected at depths of 1, 5, 10, 15, 20, 25 (Kattegat and the Belt Sea only), 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, 200, 225, 250, 300 and 400 metres; and as close to the bottom as possible.

2.3.2 Sampling method(s) and equipment

Sampling is carried out using the same technique as for oxygen. Samples are taken from ordinary water samplers immediately after the oxygen samples, using the same sampling technique. Subsamples are drawn with a flexible plastic tube attached to the water samplers reaching to the bottom of the glass bottle. Fill and overflow each bottle with at least three volumes. Make sure not to draw any air bubbles into the sample. The two reagents are added simultaneously using piston pipettes or dispensers. The tips of the pipetting devices should be close to the bottom of the bottle. The inserted stopper displaces the excess of water. Carefully avoid contact with reagent and trapping bubbles. The sample is mixed by thoroughly shaking.

If no oxygen is present, the sulphide samples should be taken first. Sulphide reacts with many metals, and the samplers should thus preferably be all-plastic.

50–100 ml oxygen bottles are recommended. Note that the amount of reagents added has to be adjusted according to the size of the bottles used. As concentrations rather than amounts are measured, no exact knowledge of the bottle volume is required.

2.3.3 Sample handling and analysis

The absorbance is measured in a spectrophotometer or a filter photometer at 670 nm. Measurements should be performed no sooner than 1 hour and no later than 48 hours after the reagent addition. The bottles should be kept in dark and any change in temperature should be avoided.

Samples that cannot be analysed within 48 hours may be preserved with zinc acetate, which precipitates the sulphide as zinc sulphide. The preserved samples can be stored for a few months, if light and temperature changes are avoided. Prior to analysis, the reagents are added in the same way as for unpreserved samples. When the bottle is turned, the precipitate dissolves easily, and the colour develops normally.

(However, according to Fonselius et al. 1999, there seems to be debate on how long the samples can be stored after addition of reagents and it will depend on the concentration. Hydrogen sulphide samples of moderate concentrations (<300 µM) may be stored for several days after adding the reagents.)

3. Data reporting and storage

The concentration of hydrogen sulphide is usually expressed as µmol l^{-1}.

Data is reported annually to the HELCOM COMBINE database, hosted by ICES.

4. Quality control

4.1 Quality control of methods

No certified reference materials (CRMs) are available for control charts. The difference between double samples in a control chart with zero as the reference line provides information on both precision and the validity of the subsampling. Ideally, the result (Sample 1 – Sample 2) should be evenly distributed around zero. Any deviations from this suggest subsampling problems. The parameter is very rarely included in interlaboratory comparison exercises, mainly due to problems in withdrawing multiple samples with the same sulphide concentration from one sample container. The relatively poor precision of the method, often 5-10 %, could probably be attributed to the combined effects of all steps in the sampling and sample pre-treatment procedure.

The following steps needs to be taken to assure the quality of the measurements:

The performance of the photometer with regard to absorbance and wavelength correctness must be checked and documented using a certified set of filters, or by an equivalent method.

The reagents must be calibrated using the procedure described in Fonselius et al. (1999). For measuring volumes in this procedure, only calibrated or class A glassware should be used. It is essential that the working solutions are freshly prepared, and that the sulphide content of the stock solution is measured, not calculated from the weighing of Na2S (as Na2S of sufficient purity is not available).

New reagents should be prepared at one-year intervals.

Very high concentrations of sulphide in certain unusually stagnant areas will cause problems. In some cases, the absorption of the sample will lie outside the working range of the spectrophotometer. Dilution of the sample is possible, but will undoubtedly introduce more uncertainty into the measurement.

Laboratories should have established a quality management system according to EN ISO/IEC 17025.

Measurement uncertainty should be estimated using ISO 11352. Estimation should be based on within-laboratory reproducibility and data from intercalibrations.

Contracting parties should follow the HELCOM monitoring guideline but minor deviations from this are acceptable if the method achieves comparable results. Validation of the adopted method needs to be performed on the relevant matrix and concentration range e.g. by taking part regularly at intercomparison studies or proficiency testing schemes."

4.2 Quality control of data and reporting

Using the method recommended in Fonselius et al. (1999), the analytical precision will be approximately ±1µmol l-1.

Data must be flagged if normal QA routines or recommended storage conditions cannot be followed.

Collected data should be checked for consistency between sampled variables (e. g. dissolved oxygen and hydrogen sulphide).

Measurement uncertainty should be estimated using ISO 11352. Estimation should be based on within-laboratory reproducibility, data from proficiency testings, IRM, and, when available, CRM.

5. Contacts and references

5.1 Contact persons

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5.2 References

Cline, J.D. 1969. Spectrophotometric determination of hydrogen sulfide in natural waters Limnology and Oceanography, 14: 454–458.

Fonselius, S., Dyrssen, D., and Yhlen, B. 1999. Determination of hydrogen sulphide. In Methods of seawater analysis, 3rd edition. Ed. by K. Grasshoff et al. Wiley-VCH, Germany.

Grasshoff, K., and Chan, K.M. 1971. An automatic method for the determination of hydrogen sulphide in natural waters. Analytica Chimica Acta, 53: 442–445.

ISO 11352*: Water quality – Estimation of measurement uncertainty based on validation and quality control data

EN ISO/IEC 17025*: General requirements for the competence of testing and calibration laboratories

* For undated references, the latest edition of the referenced document (including any amendments) applies

5.3 Additional literature

Lysiak-Pastuszak E and Krysell M (eds). Chemical measurements in the Baltic Sea: Guidelines on quality assurance.

ICES Techniques in Marine Environmental Sciences, No. 35. 149pp, ISBN 87-7482-021-4.